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(19) (CA) **CANADIAN PATENT** (12)

(54) Process for the Continuous Production of Aromatic  
Diamines with the Simultaneous Production of Steam

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**Canada**

A PROCESS FOR THE CONTINUOUS PRODUCTION OF  
AROMATIC DIAMINES WITH THE SIMULTANEOUS PRODUCTION OF STEAM

ABSTRACT OF THE DISCLOSURE

Aromatic diamines are produced on a continuous basis by the catalytic hydrogenation of a reaction suspension of an aromatic dinitro compound, an aromatic diamine corresponding to the dinitro compound, finely-divided solid hydrogenation catalyst in suspension, water and organic solvent. The hydrogenation is carried out in a reactor made up of a bubble column provided with field tubes in which water circulated to cool the reactor is converted to steam. The ratio of the cooling area of the field tubes to the reaction volume is from 40 to 400 m<sup>2</sup>/m<sup>3</sup>. An excess pressure of from 40 to 200 bars is maintained in the bubble column. The reaction temperature is from 140 to 250°C. The space-time yield per cubic meter of reaction volume is typically from 1.4 to 3.5 metric ton of diamine per hour. This process is particularly advantageous in that steam having an excess pressure of more than 1 bar is produced.

A PROCESS FOR THE CONTINUOUS PRODUCTION OF  
AROMATIC DIAMINES WITH THE SIMULTANEOUS PRODUCTION OF STEAM

BACKGROUND OF THE INVENTION

5 This invention relates to a new process for the  
continuous production of aromatic diamines with the  
simultaneous production of steam. In this process, the  
aromatic dinitro compounds which correspond to the  
diamines are catalytically hydrogenated using a bubble  
column provided with field tubes. The water which is  
10 passed through the field tubes to cool the system is  
partially converted into steam.

Many processes are known for the production of  
aromatic amines by catalytic hydrogenation of the nitro  
compounds on which they are based (see, for example  
15 German Offenlegungsschriften 1,542,544; 1,947,851;  
2,106,644; 2,135,154; 2,214,056; 2,456,308; Belgian  
Patents 631,964; 661,047; 661,946; French Patent  
1,359,438 or British Patent 768,111).

A considerable amount of heat is released during  
20 the reaction of aromatic dinitro compounds with hydrogen.  
Numerous attempts have been made to use this heat released  
during the production of aromatic diamines from the  
corresponding dinitro compounds. For example, the  
cooling water which is heated during the hydrogenation  
25 process may be used for heating rooms or for heating  
product flows, or even for the evaporation of low-boiling  
solvents. However, until now use of the heat of the  
reaction for the production of steam of more than 1 bar  
excess pressure had not been achieved. This may be  
30 attributable to the fact that there is a risk of un-  
controlled secondary reactions during the hydrogenation



of aromatic dinitro compounds. In a comparatively harmless case, such secondary reactions may result in the formation of undesired by-products and thus in reduced yields. Examples of such possible secondary reactions are: nuclear hydrogenation, hydrogenolysis or the formation of high molecular weight, tarry products. In a more serious case, explosive reactions may take place.

Another difficulty lies in the fact that the partial pressure of the hydrogen falls at elevated temperatures due to the increased partial pressures of the water of the reaction and, if appropriate, of the solvents which are simultaneously used. This is an undesirable effect which also promotes secondary reactions. Further difficulties lie in the often inadequate distribution of the hydrogen in the reaction mixture and in the coating of the cooling surfaces with resinous compounds and/or catalyst matter. In order to rule out as far as possible these undesired effects, the large-scale hydrogenation of aromatic dinitro compounds has been carried out at temperatures which are as low as possible, thereby precluding the production of steam having an excess pressure of more than 1 bar.

#### SUMMARY OF THE INVENTION

It is an object of the present invention to provide a new process for the production of aromatic diamines by hydrogenation of aromatic dinitro compounds, which process allows the production of steam having an excess pressure of above 1 bar, but which nevertheless does not suffer from the above-mentioned disadvantages.

These and other objects which will be apparent to those skilled in the art are accomplished by simultaneously introducing a reaction suspension and excess

hydrogen into the lower part of a reactor, reacting these materials and continuously removing the product aromatic diamines and excess hydrogen from the upper part of the reactor. The reactor is made up of a bubble column provided with field tubes. During the reaction, the reactor is cooled by water circulated through field tubes and through a steam separator. 10-50% of the total water fed into the field tubes is converted into steam of more than 1 bar excess pressure in the field tubes. A quantity of water corresponding to the amount of steam thus-produced is then introduced at any point downstream of the steam separator and upstream of the inlet into the field tubes. During the hydrogenation reaction, the ratio of the cooling area of the field tubes to the reaction volume is from 40 to 400 m<sup>2</sup>/m<sup>3</sup> and an excess pressure of from 40 to 200 bars is maintained in the bubble column. The quantity of reaction suspension fed into the bubble column and the pressure of the heated cooling water are regulated so that a reaction temperature of from 140 to 250°C prevails in the bubble column. The reaction suspension is made up of aromatic dinitro compounds, aromatic diamines corresponding to the dinitro compounds, finely-divided solid hydrogenation catalyst in suspension, water and organic solvent.

#### BRIEF DESCRIPTION OF THE DRAWING

The drawing is a schematic representation of an apparatus suitable for carrying out the process of the present invention.

#### DETAILED DESCRIPTION OF THE INVENTION

This invention provides a process for the continuous production of aromatic diamines with the simultaneous production of steam by catalytic hydrogenation of aromatic dinitro compounds. In this

process, a reaction suspension made up of aromatic dinitro compounds, aromatic diamines corresponding to these dinitro compounds, finely-divided suspended, solid hydrogenation catalyst, water and organic solvent is reacted with excess hydrogen. The reaction suspension and the hydrogen are simultaneously introduced into the lower part of a reactor and the end product and excess hydrogen are continuously removed from the upper part of the reactor. A bubble column (1) provided with field tubes (2) is used as the reactor. The reactor is cooled by water which is circulated through the field tubes and through a steam separator (3). 10 to 50% of the total quantity of water introduced into the field tubes is converted into steam of more than 1 bar excess pressure in the field tubes. A quantity of water corresponding to the amount of steam is supplied to the water circulation at any point downstream of the separator and upstream of the inlet into the field tubes. During the hydrogenation reaction, this ratio of the cooling area of the field tubes to the reaction volume is maintained at from 40 to 400 m<sup>2</sup>/m<sup>3</sup>. An excess pressure of from 40 to 200 bars is maintained in the bubble column. The quantity of reaction suspension introduced into the bubble column on the one hand, and the pressure (and thus the temperature) of the boiling cooling water on the other hand is calculated so that a reaction temperature of from 140 to 250°C prevails in the bubble column.

The apparatus to be used in the present process is shown schematically in the drawing. In this drawing, the reference numerals represent the following:

- (1) a bubble column,
- (2) field tubes (cooling fingers in the form of double-walled tubes) extending into the bubble column;

- (3) a steam separator;
- (4) a pump to maintain the circulation of cooling water;
- (5) a feed pipe for the reaction suspension discharging into the lower part of the bubble column;
- (6) a feed pipe for hydrogen discharging into the lower part of the bubble column;
- (7) a pipe system for the circulation guidance of the excess hydrogen;
- (8) a drain conduit for the removal of finished product suspension;
- (9) a pipeline to maintain the circulation of cooling water;
- (10) the steam removal point, and
- (11) feed pipe for the addition of fresh water into the cooling circulation.

The apparatus which is shown schematically in the drawing is useful for carrying out the process of the present invention. However, apparatus which differ substantially from this representation may also be used. Thus, for example the hydrogen or the reaction suspension need not be introduced strictly at the bottom of the bubble column. The reactant materials may also be added at any other point in the lower part of the bubble column. It would also be possible for the hydrogen to be combined with the reaction suspension just before being fed into the bubble column. Of course, the bubble column may also be provided with more than two parallel-connected field tubes. Apparatus which have from 10 to 200 parallel-connected field tubes are preferably used. The only essential factor when carrying out the process of the present invention is that the ratio of the cooling area of the field tubes to the reaction volume be from 40 to 400, preferably

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from 50 to 150 m<sup>2</sup>/m<sup>3</sup>. The bubble column generally has a volume of from 0.1 to 10 m<sup>3</sup>.

5 The reaction suspension which is introduced into the bubble column is preferably a mixture made up of from 10 to 40 (preferably from 25 to 36) parts by weight of aromatic dinitro compounds, from 5 to 20 (preferably from 7 to 15) parts by weight of aromatic diamines corresponding to the dinitro compounds, from 1.5 to 10 (preferably from 2 to 8) parts by weight of solid catalyst which is suspended in a fine distribution, 10 from 5 to 20 (preferably from 10 to 15) parts by weight of water, and from 25 to 60 (preferably from 35 to 50) parts by weight of solvent.

15 The quantity of this reaction suspension introduced into the bubble column generally corresponds to a quantity of aromatic dinitro compound (present in the reaction suspension) of from 2 to 5, preferably from 2.7 to 4.5 t/h for each cubic meter of reaction volume. The temperature of the reaction suspension at the reactor inlet is generally from about 20 to 80°C, 20 preferably from about 40 to 60°C.

The finished product suspension leaving the reactor is made up substantially of aromatic diamine, catalyst, water and solvent. The yield of the hydro- 25 genation reaction, based on dinitro compound which is used, is almost quantitative (higher than 95% of the theoretical yield).

After separating the circulated hydrogen and after relieving the pressure, the finished product 30 suspension may be freed from suspended catalyst, for example by filtration, and may then be worked up by distillation. The catalyst which is recovered may be reused. To produce the reaction suspension, some of

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the liquid phase of the finished product suspension may, if desired, be re-used before or after it has been worked up by distillation.

5 The system is cooled by water which is pumped in circulation via the field tubes (2) and the separator (3). At the inlet to the field tubes the water has a temperature of from about 70 to 165°C. From 10 to 50% of this water is converted into steam of more than 1 bar, preferably from 1.5 to 6 bars excess pressure, in the  
10 field tubes. A quantity of water which corresponds to the quantity of steam is simultaneously delivered into the cooling water circulation at any point downstream of the separator and upstream of the inlet into the field tubes.

15 Any aromatic dinitro compounds may be used in the present process. The following are examples of suitable dinitro compounds: 1,3-dinitrobenzene; 2,4-dinitrotoluene; 2,6-dinitrotoluene; commercial dinitrotoluene mixtures substantially consisting of the two  
20 last-mentioned isomers, or 1,5-dinitronaphthalene. 2,4-dinitrotoluene or commercial mixtures thereof with up to 35 wt. % (based on the total mixture) of 2,6-dinitrotoluene are more preferably used as aromatic dinitro compounds. These commercial mixtures may also contain  
25 minor quantities, (i.e. up to a maximum of 5 wt. %, based on the total mixture) of 2,3-, 2,5- or 3,4-dinitrotoluene.

Any of the hydrogenation catalysts which are known for aromatic nitro compounds may be used for the  
30 process of the present invention. The metals of the Eighth Secondary Group of the Periodic Table of Elements which may be applied, for example to carrier materials, such as oxides of magnesium, aluminum and/or silicon are particularly suitable. Raney iron, Raney  
35 cobalt and/or Raney nickel are preferably used, most

preferably, Raney nickel. The catalysts are used in a finely-divided condition and are suspended in the reaction suspension in a finely-divided manner. Maintenance of this suspension is ensured by the turbulence caused by the stream of hydrogen introduced during the process of the present invention.

Solvents which are suitable for the present process include saturated, monohydric, aliphatic alcohols having from 1 to 6 carbon atoms, such as methanol, ethanol, isopropanol or n-hexanol. Isopropanol is particularly preferred.

The hydrogen is used in a high excess, based on the dinitro compound, and is introduced into the reactor while maintaining a hydrogen pressure of from 40 to 200 bars, preferably from 70 to 120 bars.

The process of the present invention allows the production of aromatic diamines in a space-time yield per  $\text{m}^3$  reaction volume of from 1.4 to 3.5 t/h, preferably from 1.8 to 3 t/h, with the simultaneous production of steam of an excess pressure of more than 1 bar (preferably from 1.5 to 6 bars) in a quantity of from about 1 to 2.5 t per tonne of dinitro compound which is used.

Having thus described our invention, the following Example is given by way of illustration.

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#### EXAMPLE

The reactor used in this Example corresponds to that schematically represented in the drawing. The reaction volume of the bubble column was about  $0.22 \text{ m}^3$ . The reactor was provided with 37 parallel-connected field tubes which, in all, corresponded to a cooling area of about  $18 \text{ m}^2$ . The quantity of cooling water introduced into the field tube was about  $15 \text{ m}^3/\text{h}$  and the temperature of the water fed into the field tube was about  $151^\circ\text{C}$ .

3 t/h of a mixture at 55°C and made up of 33 parts by weight of dinitrotoluene (2,4/2,6-isomer mixture in a weight ratio of 80:20), 9 parts by weight of a corresponding diaminotoluene mixture, 11 parts by weight of water, 42 parts by weight of isopropanol and 5 parts by weight of finely-divided Raney nickel were conveyed into the bubble column (1) by a high pressure pump. A pressure of 100 bars was maintained in the reactor by the simultaneous introduction of hydrogen. The maximum reaction temperature in the lower third of the reactor was 220°C. A finished product suspension was continuously removed at the same time from the reactor, the quantity and diamine content of which corresponded to a yield of diamine of about 98%, based on dinitrotoluene which was used. 1.75 t/h of steam having an excess pressure of 4 bars was simultaneously removed from the system at steam removal point (10). The water corresponding to the quantity of steam was continuously delivered into the system via feed pipe (11).

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A continuous process for the production of aromatic diamines with simultaneous production of steam comprising

(A) simultaneously introducing

(i) a reaction suspension of an aromatic dinitro compound, an aromatic diamine corresponding to the dinitro compound, finely-divided suspended solid hydrogenation catalyst, water and organic solvent and

(ii) excess hydrogen

into the lower part of a reactor made up of a bubble column provided with field tubes and

(B) reacting the reaction suspension (i) with the hydrogen (ii) in a manner such that

- (a) the reactor is cooled by water circulated through the field tubes and through a steam separator with 10 to 50% of the total water fed into the field tubes being converted into steam of more than 1 bar excess pressure in the field tubes,
- (b) a quantity of water corresponding to the amount of steam is introduced at any point downstream of the steam separator and upstream of the inlet into the field tubes,
- (c) a ratio of the cooling area of the field tubes to the reaction volume is in a range of from 40 to 400 m<sup>2</sup>/m<sup>3</sup>,
- (d) an excess pressure of from 40 to 200 bars is maintained in the bubble column and
- (e) the quantity of reaction suspension fed into the bubble column and the pressure of the heated cooling water are regulated

in a manner such that a reaction temperature of from 140 to 250°C prevails in the bubble column and

(C) continuously removing the aromatic diamine product and excess hydrogen from the upper part of the reactor.

2. The process of Claim 1 in which the reaction suspension is made up of from 10 to 40 parts by weight dinitro compound, from 5 to 20 parts by weight diamine, from 1.5 to 10 parts by weight hydrogenation catalyst, from 25 to 60 parts by weight solvent and from 5 to 20 parts by weight water.

3. The process of Claim 2 in which the aromatic dinitro compound is 2,4-dinitrotoluene or a commercial mixture of 2,4-dinitrotoluene with 2,6-dinitrotoluene.

4. The process of Claim 3 in which the catalyst is selected from the group consisting of Raney iron, Raney cobalt, Raney nickel and mixtures thereof.

5. The process of Claim 3 in which the solvent is a saturated monohydric aliphatic alcohol having from 1 to 6 carbon atoms.

6. The process of Claim 2 in which the space-time yield per cubic meter of reaction volume is from 1.4 to 3.5 metric ton of diamine per hour.

7. The process of Claim 1 in which the aromatic dinitro compound is 2,4-dinitrotoluene or a commercial mixture of 2,4-dinitrotoluene with 2,6-dinitrotoluene.

8. The process of Claim 1 in which the catalyst is selected from the group consisting of Raney iron, Raney cobalt, Raney nickel and mixtures thereof.

9. The process of Claim 1 in which the solvent is a saturated monohydric aliphatic alcohol having from 1 to 6 carbon atoms.

10. The process of Claim 1 in which the space-time yield per cubic meter of reaction volume is from 1.4 to 3.5 metric ton of diamine per hour.



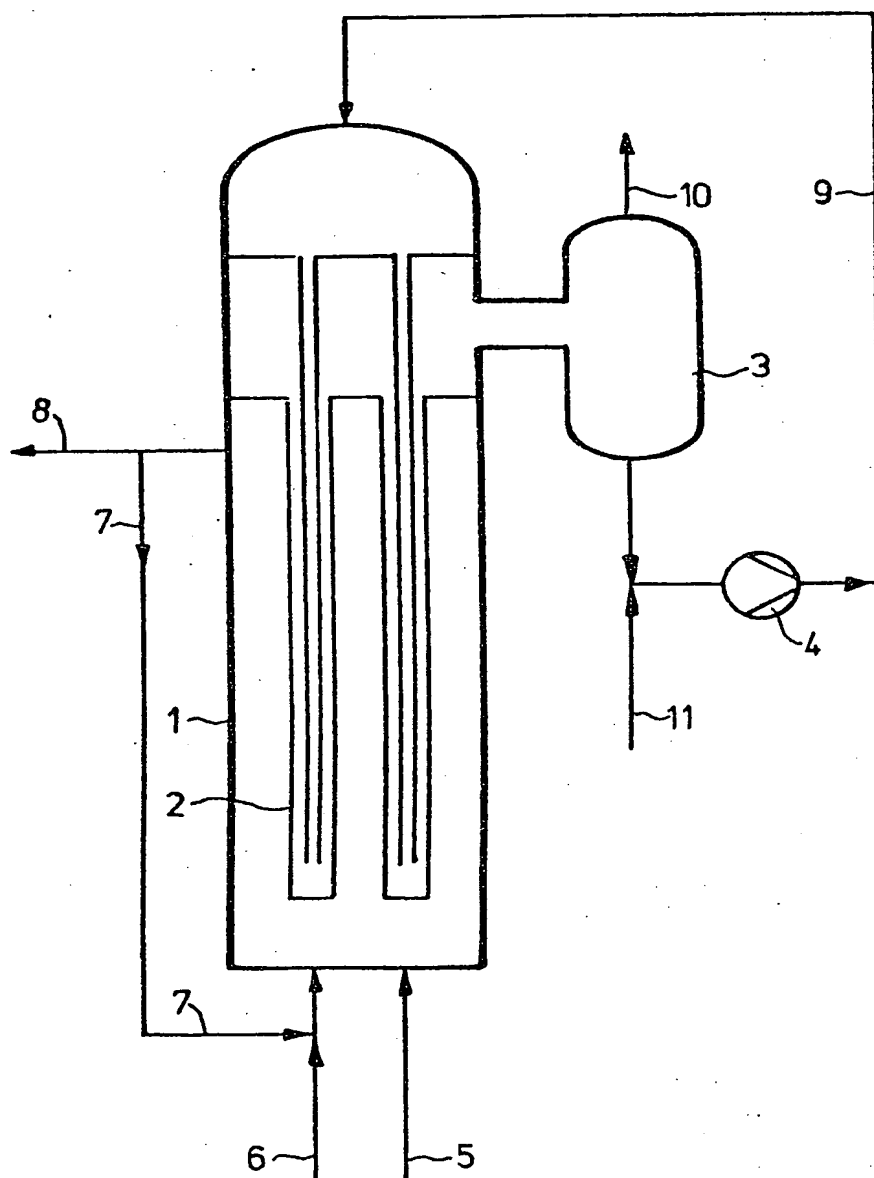


FIG. 1

*Asaboy Mitchell*  
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Agent